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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process and Apparatus for Polymerisation of Olefins

We, SOLVAY & CIE, a body corporate organised under the laws of Belgium, of 33 Rue Prince Albert, Brussels 5, Belgium, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the withdrawal of a suspension of olefin polymers in continuously operating reactors as well as to an apparatus enabling this process to be carried out.

In various continuous processes of polymerisation of unsaturated monomers, the elimination or withdrawal of the polymerised products from the polymerisation reactor is an important problem, the solution of which directly affects the good operation of the reactor as well as the production of polymers with uniform properties.

At present, in the processes usually employed, the elimination of polymerised products is very difficult and requires the withdrawal of large quantities of diluent and reactants, which must then be separated from the polymer and treated with a view to their being recycled into the polymerisation autoclave.

The process and apparatus of the present invention enable the majority of these drawbacks to be avoided.

The present invention provides a process for the withdrawal of a suspension of olefin polymers in a reactor in which the polymerisation of olefins is carried out continuously under low pressure in a diluent and in the presence of a polymerisation catalyst, comprising withdrawing a substantial amount of the crude polymer suspension from the polymerisation reactor and pouring it into a decanting zone, withdrawing from the polymer enriched broth a portion at least corresponding to the production of the polymer in the reactor, recycling to the polymerisation reactor the slightly concentrated polymer containing liquid which is extracted from the decanting zone, through a recycling conduit, and introducing, into the slightly concentrated polymer containing liquid extracted from the decanting zone, while the latter liquid is being recycled into the reactor, at least one of the constituents of the reaction medium.

A preferred feature of the process described hereinabove comprises withdrawing from the polymer enriched broth, apart from the quantity of the broth corresponding to the production of the polymer in the reactor, an additional portion which is recycled to the reactor.

As specified above, there is introduced, into the slightly concentrated polymer containing liquid extracted from the decanting zone, while the latter liquid is being recycled into the reactor, at least one of the constituents of the reaction medium; the latter constituent(s) may comprise in particular the monomer to be polymerised and if desired the balance of the diluent and a chain transfer agent, the catalyst being introduced directly into the reactor.

A further preferred feature of the process according to the present invention resides in the adjustment of the respective proportions of the polymer enriched broth and the slightly concentrated polymer containing liquid escaping from the decanting zone, by means of a regulating valve mounted in the recycling conduit for the slightly concentrated polymer containing liquid.

The invention further includes an apparatus for carrying out the above process.

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In the process and apparatus of the present invention, the amounts of unconverted monomer and suspension liquid to be dealt with before recycling into the polymerisation reactor are considerably reduced. In particular, the amount of ethylene or other olefin which, having vaporised as a result of the product being recovered at *atmospheric* pressure, has to be recompressed and purified, before it can be recycled into the reactor, is considerably reduced.

Furthermore, the apparatus according to the present invention makes it possible to predissolve in the flow of the slightly concentrated polymer containing liquid which is extracted from the separator, constituents of the reaction medium such as the monomer, the diluent and if desired a chain transfer agent under conditions under which the reaction cannot commence because of the absence of a solid catalyst from the suspension.

Such a process is especially effective in avoiding substantial variations in the concentrations of the reactants in certain parts of the reactor, which can be responsible for the formation of polymer fractions with undesirable properties.

Another arrangement applicable to the process of the present invention utilises the separator under conditions under which it provides a granulometric sorting, so as to separate a concentrated broth containing particles over a certain predetermined granule size. Smaller particles, consisting mainly of grains enriched in catalysts, are then recycled to the reactor by the circuit of the slightly concentrated polymer containing liquid.

When the operation is carried out in this manner, the productivity of the solid catalyst is improved by avoiding the loss, through premature exit from the reactor, of grains rich in catalyst which have spent very little time in the polymerisation reactor.

In such a case, however, it will be necessary to avoid predissolving the monomer or other reaction components in the slightly concentrated polymer containing liquid which is recycled into the reactor, so as to avoid the occurrence of polymerisation in the recycling pipe.

The invention is further illustrated by the following non-limitative Examples.

Example 1

For the sake of comparison with the process and apparatus of the invention and in order better to bring out its advantages, there was carried out a polymerisation experiment in which the withdrawal of the polymer suspension and the recycling of the reactants were effected in the usual manner without using the apparatus disclosed herein.

There was used a polymerisation reactor for ethylene of 200 litres capacity, completely full of liquid and thus without gaseous volume, with a concentration of ethylene in the hexane used as diluent of 3 grams per litre of hexane.

The amount of solid catalyst introduced into the reactor was 6 grams per hour.

This catalyst was constituted by the product of the reaction between Mg(OH)Cl and $TiCl_4$, obtained as described in French Patent No. 1448320. This catalyst was activated by triisobutylaluminium.

The operating pressure in the reactor was 30 kg/cm^2 and the reaction temperature was 80°C. The normal polyethylene concentration in the reactor was 0.135 kg per litre of hexane. The hourly rate of production of polyethylene was 6.750 kg/hour.

For a production rate of 6.75 kg/hour, the amount of hexane extracted from the reactor and having to be treated before being recycled into the reactor was 6.75/0.135=50 litres per hour, and the amount of non-transformed ethylene was therefore 3×50=150 grams per hour.

The amount of hexane carried away with the polyethylene was replaced by an equivalent amount, namely 50 litres per hour, of fresh solvent.

The amount of ethylene introduced into the reactor is 6.750 + 0.150 = 6.9 kg per hour. If this ethylene were pre-dissolved in the added fresh solvent, its concentration would be 6.9/50=0.138 kg/litre of hexane.

A solution of such concentration introduced at one point of the reactor would create therein a zone of significantly different concentration which would then require very vigorous agitation to reduce the extent and the concentration-difference of this high concentration zone.

Example 2

The reactor formed part of an apparatus as shown in the accompanying Figure and the operation was carried out under the same polymerisation conditions as set forth in Example 1.

The crude polyethylene suspension was drawn off by means of pump 4 which discharged 1135 litres of suspension per hour.

This suspension was then introduced into separator 6 where 500 litres of hexane per hour were separated in the form of a clear liquid containing practically no polymer.

The concentrated broth was discharged from the separator at a rate of 635 litres/hour. It consisted of 135 kg of polyethylene per hour and 500 litres of hexane per hour. For a production rate, i.e. a rate of withdrawal through valve 8, equal to that of Example 1, namely 6.75 kg of polyethylene per hour, the amount of hexane carried

invention are generally applicable to the withdrawal of polymers obtained by continuous polymerisation of olefins, and, in particular, of ethylene, propylene, butene-1, pentene-1, and 4-methyl-pentene-1, as well as by the copolymerisation of olefins with each other or with diolefins, which may be conjugated (e.g. butadiene-1,3) or non-conjugated.

The invention is applicable to the withdrawal of polymers and copolymers obtained in the form of solid particles which are not dissolved in the diluent and which result from the polymerisation of one or more olefins with the aid of any catalyst suitable for polymerisation under low pressure.

Such catalysts are, for example, catalysts containing chromium oxide which is at least partially in a hexavalent state, deposited on supports such as silicon dioxide, aluminium oxide and aluminium silicates, or catalysts resulting from the action of reducing agents on metallic compounds of the metals of groups IV A to VI A (viz. Ti, Zr, Hf, Th, V, Nb, Ta, Pa, Cr, Mo, W and U) of the Periodic Table, i.e. the Periodic Classification of the Chemical Elements according to Mendeleeff. Such catalysts are, for example, the combinations of diethylaluminium chloride or triisobutylaluminium with a titanium tetrahalide, titanium trichloride or the complex of the formula $3TiCl_3.AlCl_3$.

There can also be used high activity supported catalysts and particularly those obtained by activating by means of an organometallic compound, preferably a trialkylaluminium or an alkylaluminium halide, the product of the reaction between a compound of a transition metal and a solid support, such as, for example, a hydroxychloride of a divalent metal, particularly magnesium hydroxychloride, or an inorganic phosphate containing one or more hydroxy groups in the molecule and/or water of crystallisation. In this case, the compounds of transition metals may more particularly be halides, haloalkoxides and alkoxides of metals of the groups IV A, V A and VI A of the Periodic Table (as identified in the immediately preceding paragraph), e.g. derivatives of titanium and vanadium such as $TiCl_4$, $Ti(OC_2H_5)_4$, $Ti(OC_2H_5)_3Cl$, $VOCl_3$, VCl_5 or $VO(OC_4H_9)_3$.

The polymerisation is preferably carried out in the presence of a liquid hydrocarbon diluent which is inert under the polymerisation conditions and in which the major portion of the polymer is insoluble under the polymerisation conditions.

Suitable diluents are paraffinic hydrocarbons such as those having 3 to 8 carbon atoms in the molecule and particularly n-butane, iso-butane, n-pentane, iso-pentane and n-hexane, and cyclic saturated hydrocarbons such as cyclohexane, cyclopentane and methylcyclohexane.

A particularly suitable diluent in certain cases is the monomer itself maintained in liquid state under its saturation pressure.

The single Figure accompanying the present specification is a schematic representation of one form of apparatus suitable for carrying out the process of the present invention.

The polymerisation reactor 1, heated or cooled by means of a double jacket, is provided with a stirrer 2 capable of effecting the thorough stirring of the reaction medium, and with at least one inlet tube (not shown) for the introduction of the polymerisation catalyst.

The tube 3, provided with a pump 4, enables a substantial amount of the crude polymer suspension to be withdrawn in a continuous manner from reactor 1 and conveyed by means of tube 5 into a decanter or separator 6, which may, for example, be of a cyclone type.

A portion of the concentrated broth discharged from separator 6 is conveyed back to the polymerisation reactor 1 by means of a conduit 7, while the other portion, substantially corresponding to the polymer production of the reactor, is periodically or continuously withdrawn through the valve 9 mounted on outlet tube 8.

The slightly concentrated polymer containing suspension extracted from separator 6, on the other hand, is conveyed to the polymerisation reactor 1 by means of conduit 10 provided with a regulating valve 11, the degree of opening of which controls the degree of thickening of the concentrated suspension by the adjustment of the respective proportions of the polymer enriched broth and the slightly concentrated polymer containing liquid escaping from separator 6.

There are also provided a tube 12 and a valve 13 to allow the introduction into the slightly concentrated polymer containing liquid, while the latter is being recycled to the reactor, of constituents of the reaction medium, and particularly the monomer, the diluent and if desired a chain transfer agent, under conditions under which the polymerisation reaction cannot start because of the absence of the solid catalyst from the suspension.

As decanting means, there can be utilised, apart from separators of the cyclone type, other well-known separators such as continuously operating decanting tanks, centriclone separators or centrifuges.

As the polymerisation autoclave, there can be used any reactor operating continuously and particularly a closed circuit reactor with a continuous circulation path.

along with the polymer and therefore having to be treated before being recycled, was only $500 \times 6.75/135 = 25$ litres/hour, and the amount of ethylene which was not transformed was thus $3 \times 25 = 75$ grams/hour.

Furthermore, if the 6.825 kg of ethylene were predissolved in the 500 litres/hour of the slightly concentrated polymer containing liquid, collected from the separator and intended to be recycled into the reactor, the concentration of this solution would only be $6825/500 = 13.6$ grams of ethylene per litre.

This concentration of ethylene in the recycled hexane, which is much closer to the average concentration in the reactor, is acceptable and considerably reduces the risks of local heterogeneity in the reactor.

Of course, the amount of solvent carried along by the polyethylene can be further limited, by increasing the polymer concentration in the suspension coming out of the separator. The limit to such an increase in polymer concentration will be determined by the requirement of pumping the concentrated suspension to recycle it into the reactor.

WHAT WE CLAIM IS:—

1. Process for the withdrawal of a suspension of olefin polymers in a reactor in which the polymerisation of olefins is carried out continuously under low pressure in a diluent and in the presence of a polymerisation catalyst, comprising withdrawing a substantial amount of the crude polymer suspension from the polymerisation reactor and pouring it into a decanting zone, withdrawing a portion of the polymer enriched broth at least corresponding to the production of the polymer in the reactor, recycling to the polymerisation reactor the slightly concentrated polymer containing liquid which is extracted from the decanting zone, through a recycling conduit, and introducing, into the slightly concentrated polymer containing liquid extracted from the decanting zone, while the latter liquid is being recycled into the reactor, at least one of the constituents of the reaction medium.

2. Process according to Claim 1, in which the polymer enriched broth is withdrawn in an amount corresponding to the production of the polymer in the reactor with a further portion being withdrawn for recycling into the reactor.

3. Process according to Claim 1 or 2, in which the constituent introduced into the slightly concentrated polymer containing liquid while the latter is being recycled into the reactor is the monomer to be polymerised.

4. Process according to Claim 1 or 2, in which the constituents introduced into the slightly concentrated polymer containing liquid while the latter is being recycled into the reactor are the monomers to be polymerised, the remainder of the diluent required and a chain transfer agent, the polymerisation catalyst being introduced directly into the reactor.

5. Process according to Claim 1, in which the respective proportions of the polymer enriched broth and the slightly concentrated polymer containing liquid escaping from the decanting zone are adjusted by means of a regulating valve mounted in the recycling conduit for the slightly concentrated polymer containing liquid.

6. Apparatus for polymerisation of olefins and withdrawal of the resulting suspension of olefin polymers comprising: a continuously operating polymerisation reactor; a decanter for the crude polymer suspension; means for transferring the crude polymer suspension from the reactor into the decanter; means for withdrawing polymer enriched broth from the decanter and a recycling conduit from the decanter to the reactor for recycling into the reactor the slightly concentrated polymer containing liquid, this recycling conduit being provided with inlet means for the introduction of reaction constituents.

7. Apparatus according to Claim 6, further comprising a recycling conduit from the decanter to the reactor for the polymer enriched broth.

8. Apparatus according to Claim 6, in which the recycling conduit for the slightly concentrated polymer containing liquid is provided with a flow regulating valve.

9. Process according to Claim 1, substantially as hereinbefore described with reference to the accompanying drawing and/or in the foregoing Example 2.

10. Apparatus according to Claim 6, substantially as hereinbefore described with reference to the accompanying drawing.

11. Olefin polymers and copolymers obtained by a process as claimed in any of Claims 1 to 5 and 9.

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1 SHEET

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